

## Preliminary Note

### Photophysics and photochemistry of cyclic unsaturated $\alpha$ -diketones

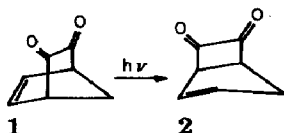
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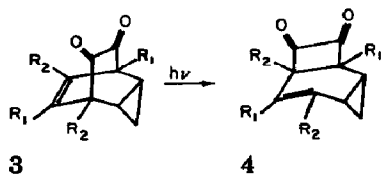
(Received March 21, 1984; in revised form May 4, 1984)

#### 1. Introduction

We have previously reported [1] results relating to the competition between photochemical isomerization  $1 \rightarrow 2$



and fluorescence decay of the unsaturated diketone 1 (at 436 nm). Similar studies with the norcaradiene precursors [2, 3] 3 now show that wavelength and structure effects play a significant role in such competitions:



- a,  $R_1 \equiv R_2 \equiv H$   
 b,  $R_1 \equiv H, R_2 \equiv \textit{tert}$ -butyl;  $R_1 \equiv \textit{tert}$ -butyl,  $R_2 \equiv H$   
 c,  $R_1 \equiv R_2 \equiv Cl$

#### 2. Experimental details

The main features of the experimental set-up and experimental procedure have been described earlier [1]. A tunable dye laser (Molelectron DL 200) was used to study the excitation wavelength effects. The photochemical actinometer developed by Heller [4] and modified by Rubin [5] was used. Solutions of 1a and 3c were prepared using 2-methyltetrahydrofuran; the other compounds were dissolved in a 1:1 mixture of methylcyclohexane and isopentane. The solvents were purified by passing them through a column of activated alumina.

### 3. Results and discussion

Photochemical isomerizations [2, 3] of unsaturated diketones **3** to unsaturated cyclobutanediones **4** proceeded quantitatively (excitation at 404 nm or 436 nm using diphenylstilbene and Coumarin 120 laser dyes respectively) at room temperature in a variety of aprotic solvents; the quantum yields (excitation at 436 nm; room temperature) were 0.47, 0.21 and 0.65 respectively for **3a**, **3b** and **3c**. Investigation of the temperature and the excitation wavelength dependence for quantum yields of the photoisomerization and of the competing fluorescence of **3a** - **3c** leads to the following observations.

(1) The quantum yields for reaction of **3a** (Fig. 1) and of **3b** (Fig. 2) decreased with decreasing temperature and, at 436 nm, were virtually zero at 123 K. This effect was less dramatic at 404 nm and 123 K where the quantum yields for **3a** and **3b** were about 0.08 and about 0.01 respectively of the room temperature value.

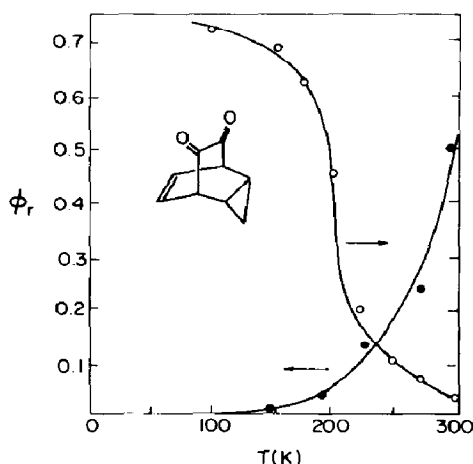


Fig. 1. Relative fluorescence quantum yield  $\phi_f$  ( $\circ$ ) and photochemical quantum yield  $\phi_r$  ( $\bullet$ ) as a function of temperature for diketone **3a** excited at 436 nm.

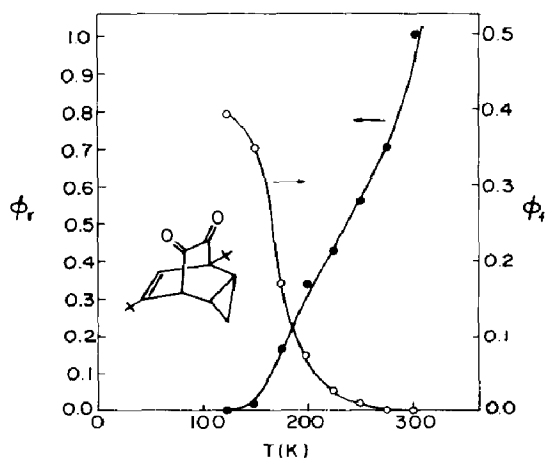


Fig. 2. Relative fluorescence quantum yield  $\phi_f$  ( $\circ$ ) and photochemical quantum yield  $\phi_r$  ( $\bullet$ ) as a function of temperature for diketone **3b** excited at 436 nm.

(2) Parallel to these decreases in reaction quantum yield, corresponding increases in fluorescence quantum yields were observed at 404 and 436 nm. Again, the temperature dependence at the shorter wavelength was less marked (Fig. 3). In contrast, the tetrachloro compound **3c**, which rearranged to **4c**, did not show a significant temperature dependence for reaction or for competition with fluorescence.

These results can be interpreted in terms of general theories pertaining to temperature-dependent radiative and non-radiative transitions [6] in addition to thermally activated photochemical reactions [7]. It is evident that photoisomerization and fluorescence decay are two competing processes for deactivating the excited electronic states of the  $\alpha$ -diketones. However, a simple competition process cannot account for the fact that at low temper-

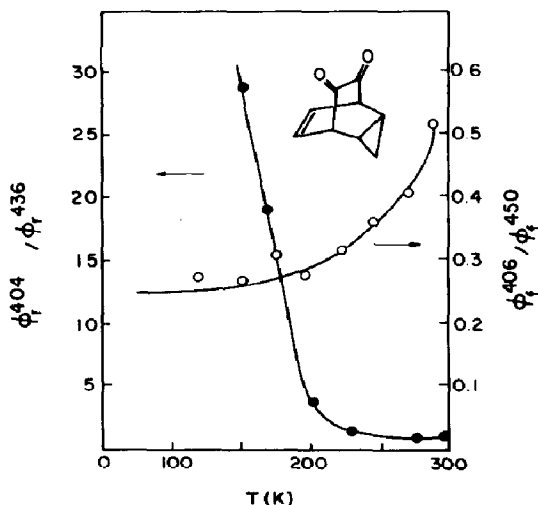


Fig. 3. Wavelength dependence of  $\phi_f$  (○) and  $\phi_x$  (●) as a function of temperature for diketone 3a.

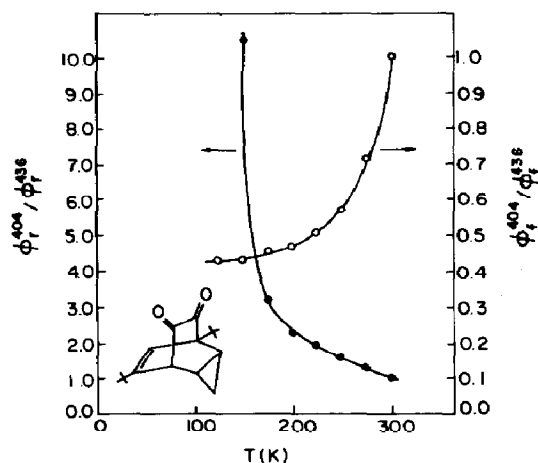


Fig. 4. Wavelength dependence of  $\phi_f$  (○) and  $\phi_x$  (●) as a function of temperature for diketone 3b.

atures the sum of the photochemical quantum yield  $\phi_x$  and the fluorescence quantum yield  $\phi_f$  is a decreasing function of temperature. We have shown [1] that a model which incorporates an activation barrier both for the photoisomerization reaction and for thermally enhanced non-radiative decay yields the following results for the quantum yields  $\phi_x$  and  $\phi_f$ :

$$\ln\left(\frac{\phi_x \phi_0}{\phi_f}\right) = \ln(\tau k_x) - \frac{\Delta E_x}{RT} \quad (1)$$

$$\ln\left\{\frac{\phi_0(1 - \phi_x)}{\phi_f - 1}\right\} = \ln(\tau k_{\text{vib}}) - \frac{\Delta E}{RT} \quad (2)$$

Here  $\phi_0$  and  $\tau$  are the fluorescence quantum yield and the fluorescence lifetime respectively at 0 K,  $\Delta E_x$  is the activation barrier for photoisomerization, which proceeds at a rate  $k_x \exp(-\Delta E_x/RT)$ , and  $\Delta E$  is the energy of vibrational excitation involved in the vibronically induced non-radiative decay for which  $k_{\text{vib}}$  is the decay rate at 0 K.

A fit of the data of Fig. 2 to eqns. (1) and (2) for the reactions of 3a and 3b yields the values for  $\Delta E$  and  $\Delta E_x$  shown in Table 1. The results indicate a structure dependence of the photochemical and photophysical properties of unsaturated  $\alpha$ -diketones. At very low temperatures, excitation at short wavelength compensates to some extent for the lack of thermal activation, thus resulting in a more moderate temperature dependence at short excitation wavelengths (Figs. 3 and 4). Fluorescence decay of the same excited state competes with the reaction while non-radiative decay of this state is more pronounced at high temperatures and at shorter excitation wavelengths. Lack of these features, as is the case with 3c, corresponds to

TABLE 1

Activation energies for the temperature-dependent photoisomerization and the fluorescence decay of unsaturated  $\alpha$ -diketones

Compound	$\lambda_{\text{exc}}$ (nm)	$\Delta E_{\text{r}}$ (kcal mol <sup>-1</sup> )	$\Delta E$ (kcal mol <sup>-1</sup> )
<b>3a</b>	404	2.09 ± 0.19	2.73 ± 0.29
<b>3b</b>	404	3.83 ± 0.12	4.40 ± 0.10
<b>3a</b>	436	4.90 ± 0.35	3.60 ± 0.10
<b>3b</b>	436	5.30 ± 0.23	4.44 ± 0.21

photoisomerization proceeding along a potential surface with a very low activation barrier. The main features of the temperature-dependent phenomena observed here are in agreement with those of other reported temperature-dependent photophysics [8] and competing photochemical and fluorescence decay studies [9].

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